Short communication

Effect of halides ions on H_2 production during aluminum corrosion in formic acid and using some inorganic inhibitors to control hydrogen evolution

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HIGHLIGHTS

- H_2 production by aluminum corrosion in formic acid in the presence of halide ions.
- Increasing acid, halides ions concentrations and temperature enhance H_2 production.
- The addition of tungstate, molybdate and nitrite anions retard H_2 production.
- SEM and EDX analysis confirm the data obtained from hydrogen evolution measurements.

GRAPHICAL ABSTRACT
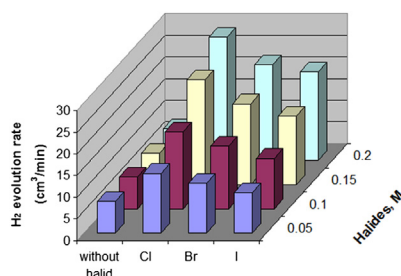
ABSTRACT

This study reports on the systematic assessment of H_2 production by corrosion of aluminum in formic acid solution in the absence and presence of halide ions and some inorganic inhibitors using hydrogen evolution measurements and complemented by scan electron microscope (SEM) and energy dispersive X-ray (EDX). It is shown that the rate of H_2 production and in turn the dissolution of aluminum increases with increasing acid concentration and solution temperature. Addition of halides ions enhances the active dissolution of aluminum and tends to breakdown the passive film and increases H_2 production. The addition of tungstate, molybdate and nitrite anions to (1.0 M formic acid + 0.2 M Cl$^-$) solution retard the rate of H_2 production, where the H_2 production process decreases in the following in the order: tungstate > molybdate > nitrite.

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1. Introduction

Several investigations about new energy sources have been carried out during the last decades [1–3]. Concerns about a possible depletion of petroleum, coal and gas, as well as new methods to achieve a more reasonable use of these raw materials to obtain energy have been widely investigated at present, especially some studies about the reduction of green house gases. The hydrogen has a very high combustion heat, which is a promising alternative in terms of energy. The concept of producing hydrogen by the reaction of certain metals with acids has intrigued researchers for many years [4–6]. Most research on producing hydrogen done by the corrosion reaction of aluminum with mineral acids [7,8]. Despite the importance of organic acids in industry, few corrosion studies involving these acids have been made. However, at high temperatures, these acids can dissociate, forming more aggressive ions that

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can cause faster corrosion than might otherwise be expected [8,9]. Formic acid is the most corrosive of the common organic acids. However, no systematic study of the corrosion behavior of aluminum in formic acid solution has been found in the literature. In formic acid, aluminum or its alloys dissolve quickly (especially at higher temperatures) according to the overall reaction:

$$2Al + 6HCOOH \rightarrow 2Al(COOH)_3 + 3H_2\uparrow \qquad (1)$$
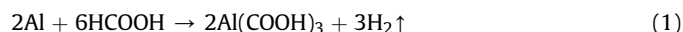
The addition of halide ions in metal/acid system causes destabilize the iron passive film [10]. They influence the chemical, ionic and electronic properties of the oxide. It has been proposed that halides ions interact with the oxide layer preferentially at local sites. This interaction results in the film breakdown and initiation of pitting corrosion [11].

The work described in this paper was undertaken to apply the hydrogen evolution measurements to study hydrogen production during aluminum corrosion in formic acid. It was also the purpose of the present work is to use some halides ions as aggressive ions for increasing hydrogen production. The role of some inorganic anions to control the H_2 production process was also investigated.

It should be noted that the corrosion reaction of aluminum with formic acid cannot be considered as a primary source of H_2 gas. That is because the production of aluminum metal requires a much greater energy input than other, more direct means of producing H_2 (e.g. electrolysis of water, cracking of hydrocarbons or the water gas reaction). However, the corrosion reaction of aluminum with formic acid reaction might be a convenient way to generate H_2 for portable applications, particularly small H_2 fuel cells.

2. Experimental

Corrosion tests were performed on aluminum sheets of the following percentage composition: Al (99.89%), Si (0.03%), Cu (0.02%), Mg (0.03%) and Zn (0.01%). Prior to each experiment, the aluminum electrodes were first briefly ground with different grades of emery paper (120, 400, 800, 1000 and 1200) and washed thoroughly with distilled water and degreased with acetone.

The apparatus and procedure followed for hydrogen evolution measurements were similar to that earlier reported [12,13]. A simple diagram showing the apparatus used to generate and measure evolved H_2 gas is shown in Fig. 1. In hydrogen evolution method, 100 ml of the corrodent (formic acid) was introduced into the reaction vessel and aluminum sheets of dimensions 4 cm × 5 cm were carefully dropped into the test solution of formic acid and the reaction vessel was quickly closed to avoid any escape of hydrogen gas. The volume of hydrogen gas evolved from the corrosion reaction was monitored by the depression (in cm^3) in the paraffin oil level. This depression was monitored at fixed time intervals. From the volume of hydrogen gas evolved, the hydrogen evolution rate (which can be correlated to corrosion rate) was calculated using the following expression [12]:

$$R_H = (V_t - V_i)/(t_t - t_i) \qquad (2)$$

where V_t and V_i are the volumes of hydrogen evolved at time t_t and t_i, respectively.

All the solutions were prepared from analytical grade reagents and distilled water. All chemicals were used as received without further purification. Formic acid (Merck) of AR grade was used for preparing solutions. The temperature of the test electrolyte was controlled by immersing the cell in a water thermostat.

The morphology of the aluminum surface of some samples was determined after the desired tests by employing scanning electron microscopy. SEM was performed using a JEOL/Quantek detector.
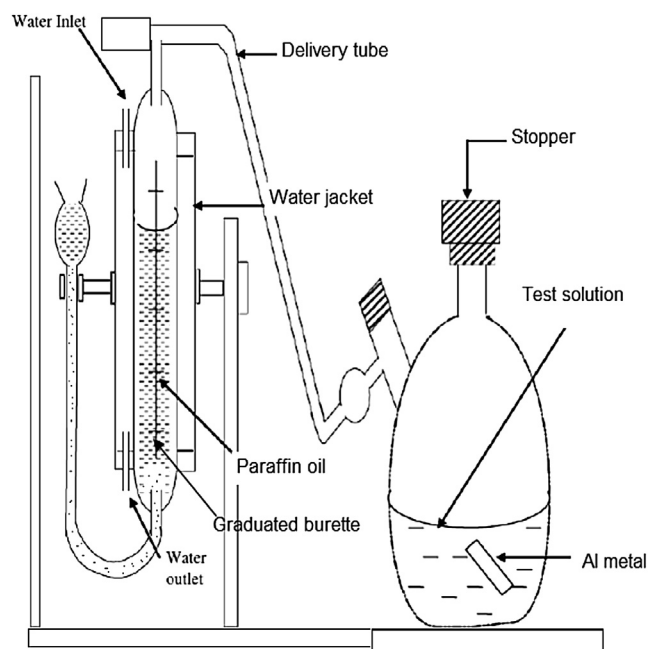

Fig. 1. Gasometric assembly for measurement of hydrogen gas evolved.

The composition and structure of the passive film formed on the electrode surface was examined by energy dispersive X-ray (EDX) investigations. The system used for this analysis was (philips p.w. Model No. 1730) with Cu−K radiation and nickel filter. It was adopted at 40 kV and 25 mA current.

3. Results and discussion

3.1. Effect of formic acid and temperature

Fig. 2 shows the hydrogen evolution rate during the corrosion reaction of aluminum electrode in formic acid solutions measured as a function of acid concentration at 25 °C. Inspection of the figure reveals that the hydrogen evolution rate increases with increase in formic acid concentration (from 0.2 to 1.0 M), indicating
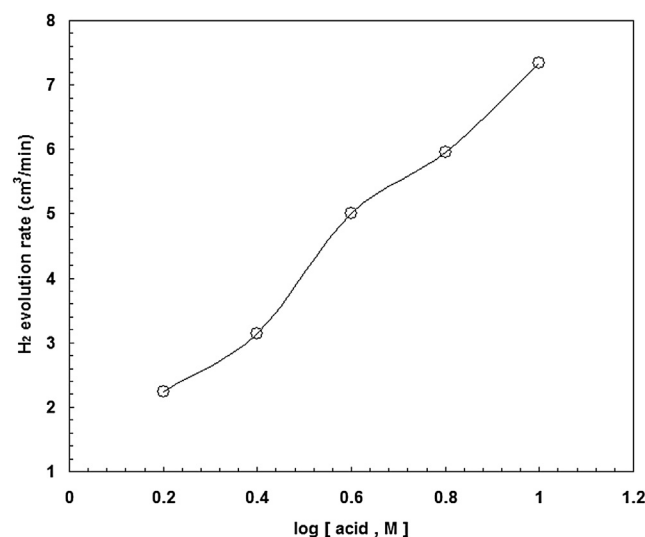

Fig. 2. Relation between H_2 evolution rate vs. formic acid concentration for aluminum at 25 °C.
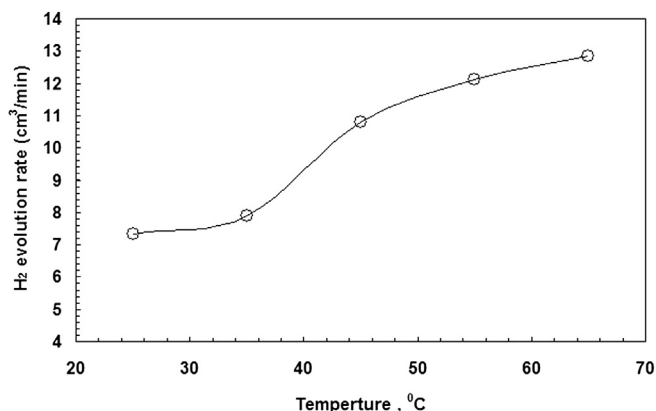
Fig. 3. Relation between H_2 evolution rate vs. temperature for aluminum in 1.0 M formic acid solution.

acceleration behavior for the aluminum dissolution. The evolution of hydrogen occurs by the following mechanism [14]:

$$2Al \rightarrow 2Al^{+3} + 6e^- \text{ (Anodic reaction)} \qquad (3)$$

$$6HCOOH + 6e^- \rightarrow 3H_{2(g)}\uparrow + 6(HCOO)^- \text{ (Cathodic reaction)} \qquad (4)$$

$$2Al + 6HCOOH \rightarrow 3H_{2(g)}\uparrow + 2Al(HCOO)_3$$
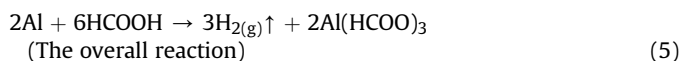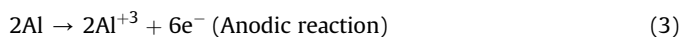$$\text{(The overall reaction)} \qquad (5)$$

Fig. 3 displays the influence of temperature (25–65 °C) on the hydrogen evolution rate during the corrosion reaction of aluminum in 1.0 M formic acid solution. It is clear from Fig. 3 that the rate of hydrogen evolution and in turn the dissolution of aluminum increases with increasing solution temperature. This indicates that higher temperatures enhance the hydrogen evolution reaction. This behavior may be attributed to an increase in solubility of oxide film with temperature. In addition, an increase in temperature accelerates the rates of diffusion and migration of the reactant and product species. Ultimately, this leads to an increase in the rate of hydrogen evolution reaction [15].

3.2. Effect of halides ions

Fig. 4 represents the hydrogen evolution rate during the corrosion reaction of aluminum in 1.0 M formic acid solution in the absen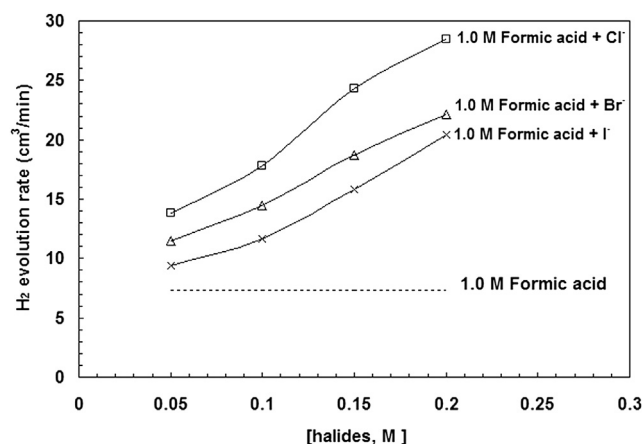ce and presence of various concentrations of halides ions at 25 °C. Results shown in Fig. 4 clearly indicate that the hydrogen evolution rate during the corrosion reaction of aluminum in 1.0 M formic acid solution was found to increase in the presence of halides ions compared to its absence. This is an indication that halides ions accelerate the rate of hydrogen evolution and in turn the rate of aluminum dissolution. This behavior could be ascribed to adsorption of halides ions (X^-) on the oxide/solution interface under the influence of electric field (at the oxide/solution interface) in competition with $(HCOO)^-$ [16]. The adsorption process is followed by chemical reaction between the adsorbed halides ions and aluminum oxide cations on the hydrated oxide surface. These processes lead to the formation of AlX^{-3} complexes. The soluble complexes immediately separate from the oxide lattice and readily go in solution and this leads to increase the metal dissolution and enhances the rate of hydrogen evolution [17]. It is also seen that the hydrogen evolution rate increases with increase in halides ions concentration. At the temperatures studied, the increasing in the hydrogen evolution rate in the presence of the halides ions was found to be in the order: $Cl^- > Br^- > I^-$. These results indicate that Cl^- ion is the most aggressive anion, while I^- is the least aggressive one. In spite of the fact that Br^- and I^- are more polarizable and hence more adsorbable than Cl^- ion, the ionic radius of halide ions seems to be an important parameter since the ionic radii increase in the order: $Cl^- < Br^- < I^-$ [18]. Therefore, it is reasonable to assume that the smaller the size of the aggressive ion, the higher is its ability to breakdown the passive layer. On the basis of the small size of Cl^- ion as compared to Br^- and I^-, the higher ability to breakdown the passive layer [19].

3.3. Effect of inorganic anions

The effect of adding different concentrations of tungstate, molybdate and nitrite anions on the hydrogen evolution rate during the corrosion reaction of aluminum in 1.0 M formic acid solution in presence of 0.2 M of chloride ions solution was investigated and presented in Fig. 5. The data show that the presence of these anions (tungstate, molybdate and nitrite) inhibits both the H_2 production and pitting corrosion of aluminum in formic acid solution. This is clearly seen from the decrease in the hydrogen evolution rate. The inhibition effect of these inhibitors on H_2 production process decreases in the order: tungstate > molybdate > nitrite.

The inhibition effectiveness of these anions may be associated with their polarizability, which gives a measure of their electrical
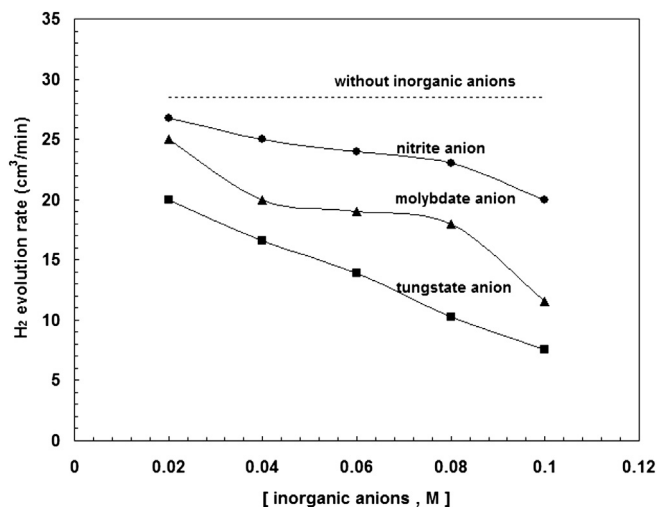

Fig. 4. Relation between H_2 evolution rate vs. halides ions concentration for aluminum in 1.0 M formic acid solution at 25 °C.

Fig. 5. Relation between H_2 evolution rate vs. inorganic anions concentration for aluminum in (1.0 M formic acid + 0.2 M Cl^-) solution at 25 °C.
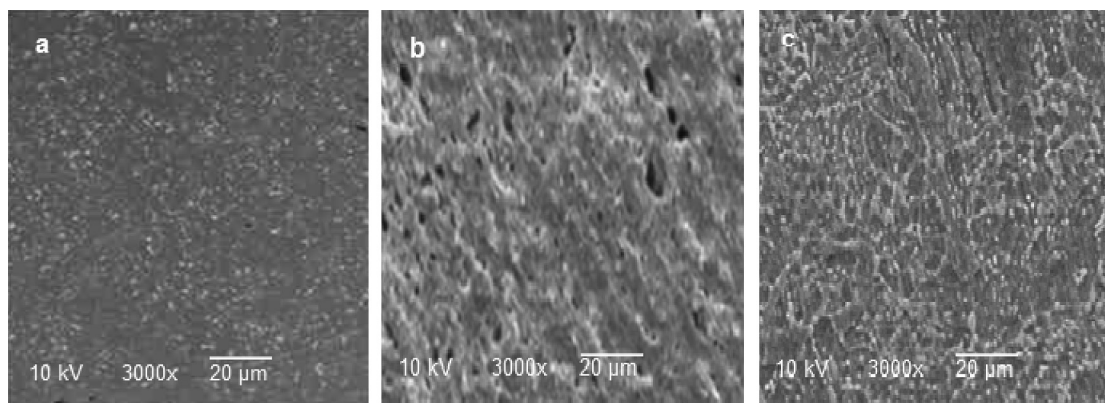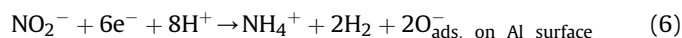
Fig. 6. SEM examination of aluminum surface in (a) 1.0 M formic acid, (b) 1.0 M formic acid + 0.2 M Cl⁻ and (c) 1.0 M formic acid + 0.2 M Cl⁻ + 0.1 M tungstate anion.

deformability [20]. The polarization of the cited anions decrease in the sequence: tungstate > molybdate > nitrite.

Since the polarizability of an anion can be assumed to be directly related to its adsorbability [21], it can be concluded that the inhibition influence of these inhibitors is due to their adsorption on the electrode surface. The anions that are strongly adsorbed on the electrode surface act as effective inhibitors. The decrease in H_2 production and in turn pitting corrosion of aluminum in formic acid solution in the presence of chloride ions upon adding increased concentrations of the inhibitive anions, could be explained in terms of the oxide film theory of passivity proposed by Hoar et al. [22] as due to the penetration of the inhibitive anions through the oxide film on the metal surface, contaminating the oxide film making it a better ionic conductor, thereby, favoring oxide growth and pitting inhibition. On the other hand, Leckie and Uhlig [23], attribute this behavior to the competitive adsorption of the inhibitive anions with the Cl⁻ ions on the surface of aluminum, thus preventing the Cl⁻ ion from the sites through which it preferentially adsorbs on the passive film and therefore decreases the tendency for pitting corrosion. In addition, W^{6+} in tungstate anion and Mo^{6+} in molybdate anion may undergo reduction into W^{4+} and Mo^{4+}, respectively, during film formation [24]. The reduced forms of these inhibitors (WO_2 and MoO_2) for instance, become part of the passivating oxide, and tend to plug its pores and flaws, thereby imparting it better protective properties.

It is probable that the role of nitrite anion in the inhibition of pitting corrosion may be due to the fast reduction of $(NO_2)^-$ to

$(NH_4)^+$ during the aluminum dissolution reaction (Equation (6)), the residual oxygen on the aluminum surface triggering the oxidation of aluminum to give aluminum oxide [24].

$$NO_2^- + 6e^- + 8H^+ \rightarrow NH_4^+ + 2H_2 + 2O_{ads.\ on\ Al\ surface}^- \qquad (6)$$

3.4. SEM and EDX analysis

Scanning electron microscopy SEM examination of aluminum surface immersed in 1.0 M formic acid solution in the presence of 0.2 M of chloride ions free from and containing different inorganic anions was carried out. In the absence of chloride ion and inorganic anions, the data show that the surface was covered with a high density of corrosion products as shown in Fig. 6a. However, in the presence of chloride ion, surface was covered with a high density of pits as shown in Fig. 6b. On other hand, in the presence of tungstate anion (as an example) the data gave no evidence of pitting and formation of adsorbed film on aluminum surface (Fig. 6c). This may be interpreted as adsorption of these inhibitor anions on the passive film. These adsorbed anions become part of the passivating oxide, and tend to plug its pores and defect sites, therefore imparting it better protective properties.

Further insight into the processes occurring at the aluminum surface in 1.0 M formic acid solution containing of 0.2 M of chloride ion in the absence and presence of tungstate anion (as an example) was enabled by EDX data as shown in Figs. 7 and 8 respectively. For the electrode without tungstate anion treatment (Fig. 7), Al and O
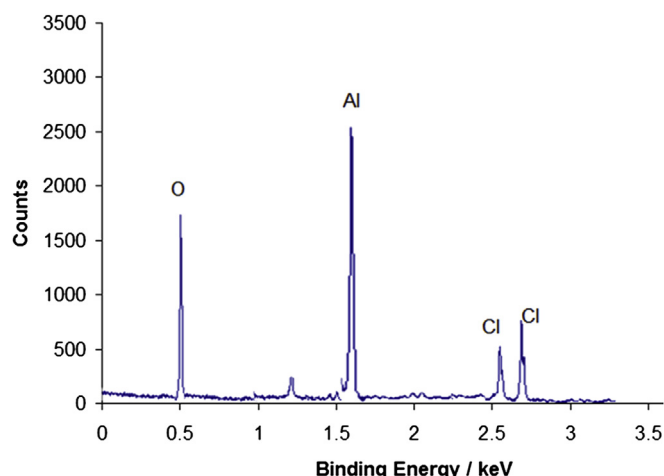

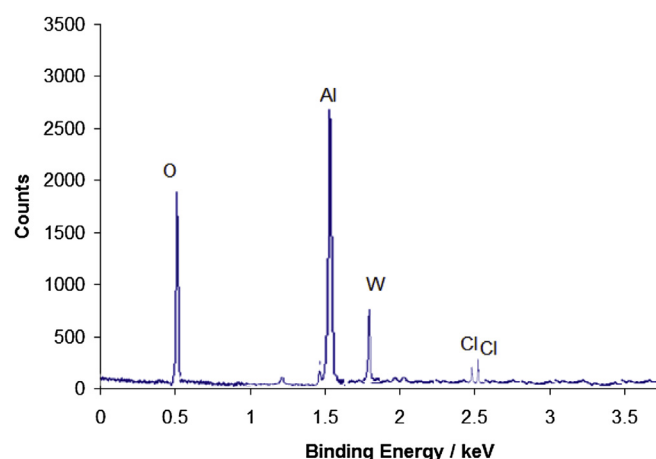**Fig. 7.** EDX spectra of aluminum surface in (1.0 M formic acid + 0.2 M Cl⁻) solution.

Fig. 8. EDX spectra of aluminum surface in (1.0 M formic acid + 0.2 M Cl⁻ + 0.1 M tungstate anion) solution.

signals were detected, which indicated that the passive film contained only Al_2O_3. In addition, a Cl signal was observed on the Al surface, reflecting the strong adsorption of Cl^- to the aluminum surface. On the other hand, the EDX spectra (Fig. 8) recorded for aluminum in (1.0 M formic acid + 0.2 M Cl^-) solution containing 0.1 M tungstate anion showed additional signal characteristic for the existence of W on the passive film and formation of a protective layer. This causes a decrease in the corrosion of aluminum in corrosive medium and consequently led to suppress in the rate of hydrogen evolution.

4. Conclusion

- Hydrogen evolution measurements and SEM and EDX analysis adopted to investigate the hydrogen production during aluminum corrosion in formic acid solution in the absence and presence of halide ions and some inorganic inhibitors.
- The rate of hydrogen evolution and in turn the dissolution of aluminum increases with increasing acid concentration and solution temperature.
- The addition of halides ions shows to contribute to an increase of the aluminum corrosion and to an accelerating effect on the rate of hydrogen evolution.
- The addition of tungstate, molybdate and nitrite anions to (1.0 M formic acid + 0.2 M Cl^-) solution retard the rate of hydrogen evolution and in turn the dissolution of aluminum, where the H_2 production process decreases in the following in the order: tungstate > molybdate > nitrite.
- It is worth noting the importance of employing complementary surface analysis techniques such as SEM and EDX in the

characterization the processes occurring at the aluminum surface.

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